Toxic Metals in Paper and Paperboard Food Packagings

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This study characterized the structure of food packages, determined the amount of toxic metals that pass through the package (due to the package's condition and contact with food), and examined the appropriateness of current food legislation. The food packages were examined for weight, ash content, and optical properties under two different light sources. The toxic metal quantities of the packages were analyzed with the use of an inductively coupled plasma optical emission spectrometry (ICP-OES). In all packages, Pb migrated into food and was found at levels that exceeded limit values. Although the amounts of Hg within the material structure were above limits in most packages, it did not migrate from the packages. Although the amount of Cd in structural packaging did not exceed the limit values, most of the migration-related values were high. The Zn concentration in packaging was substantially higher than the amount due to migration. Structural Cu values were mostly below the limit values, except in corrugated boards. Cr amounts in both packaging structure and migration were below the limit values. In all packaging, there were minimum amounts of Ni among paperboard samples and maximum amounts among corrugated boards. Al values were high among structural paper packages, as well as in migration values in paperboard packaging.

Keywords: Toxic metals; Heavy metals; Migration; Food packaging; Paper; Paperboard; Corrugated board

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INTRODUCTION

Packaging generally has the basic functions of protection, containing, and informing. In addition to these functions of food packaging, it is important for it to become a container that transports the food from the vendor to the table. It becomes both a package and at the same time a plate used on the table by preserving taste, smell, warmth, and freshness of the food in this process. During this function, it is expected that no contaminants and toxic components migrate into the food through the contact of the food with the structure of the packaging. Food packaging products containing end consumer usage areas include convenience food packages such as lahmacun, pita and pizza, tea bags, baking papers, coffee filters, wrapped solid fat packaging, sugar bags, dry packaging, and frozen food packaging, which directly get into contact with the food substances. These packaging products include paper, paperboard, and corrugated board-based substrates processed with operations such as coating, sizing which have various and different characteristics depending on the field of use.

The structure of the paper is formed from pulp that may contain virgin fiber, recycled fiber, or portions of each. The virgin pulp production and bleaching process forms mainly the basic production processes and chemical components of the paper used in these processes. In the next stage, sizing, coating, and printing operations are applied as finishing processes to the basic paper (Caner *et al.* 2006). In this processing stage, dyes, pigments, paper reinforcing chemical agents, and ink components are added to the structure of paper (Caner *et al.* 2006). Being different from the virgin fiber-containing pulp, the basic components of the pulp containing recycled pulps include filler agents coming from virgin pulp, opacity and coloring pigments and dyes, binding components, and printing ink ingredients in addition to the pulp containing recycled fibers In order to improve the resistance and other properties of the paper, recycled base paper is produced with the chemical additives used. In order to improve the surface characteristics of recycled base paper, the process includes sizing, paper coating, dyeing, and the chemical components of printing inks are incorporated as contaminants and toxic components (Binderup *et al.* 2010).

Paper and paperboard materials that are laminated with aluminum and plastic layers are used widely in food packages. According to EU-15 (2003), it is estimated that the per capita amount of coated paperboard packaging in direct contact with food is 4.4 kg (17%). The majority of this amount (70 to 80%) consists of milk and drink liquid paperboard packaging (Heikkla and Rajala 2000; The European paper and board food packaging chain 2012; Castle 2014).

Mineral materials called fillers are present in the structure of the paper by addition to the fiber suspension and surface coating in order to improve the appearance and qualities of the of paper and paperboard. Fillers can contribute as partial barriers to prevent migration and to preserve flavor, aroma, and freshness of the beverage liquids and similar food with oil, salt, and flavoring in the packages. Fillers may comprise up to 25% of the weight, depending on the type of paper produced. The main functions of fillers used in paper are listed below:

- Increase in opacity, paper dimensional stability, and whiteness.
- Printing quality may be improved due to the smoother surface that can be achieved with the use of fillers.
- The addition of calcium carbonate filler, by increasing the pH of paper forming, tends to reduce the rate of degradation of paper properties due to aging.
- Colorants used to improve properties of optic and surface include impurities such as heavy metals such as Pb, Hg, Cd, and Cr due to the chemicals composing them.

Laminated paper, which includes zinc sulphide, zinc oxide, and also the combination of lithopene (zinc sulphide in combination with barium sulphate), increases the quality of paperboard products and wall paper (Bostancı 1987; Vaarasalo 1999; Erkan and Malayoğlu 2001; Mauriello *et al.* 2004; Conti 2007, 2008).

Optical characteristics tests, which give CIE whiteness (*W*) and ISO brightness, are used to measure the attractiveness of paper. Fluorescent whiteners are highly effective and practical materials in developing paper attractiveness (Aksoy *et al*. 2003; Hubbe *et al.* 2008; Coppel 2010; Kim *et al.* 2017; Sönmez 2017). In paperboard food packaging, the printing methods and their inks are very important in their role of providing food-related information, promotional text and images, and functionality of the packaging. The structure of the printing ink varies according to the printing method. Mainly offset, gravure, and flexographic printing methods are used on food packaging. The main structure of the printing ink consists of colorants, insoluble organic and inorganic pigments, and soluble dyes. The printing ink supplementary materials are formed by the polymers and solvents used to bond or fix the ink pigments on the submaterial (Martin-Dias 1994; Mertoğlu-Elmas 2017; Sönmez 2017).

Studies have been made on the adjustment of the amount of toxic metals resulting from pigments forming colors in printing ink prescriptions. A change was found in the direction of decrease or increase in toxic metals existing as impurity in the chemical structure of components forming colors in the development of printing ink prescriptions. This change showed that printing inks can be regulated to remove toxic metals (Sutter 1994; Mertoğlu-Elmas 2017). In another study, red, blue, green, yellow, black, and white colour tones of tattoo inks were found to include toxic metals (Pb, Hg, Zn, Cd, Cu, Ni). Toxic metal values exceeding a maximum limit of Epa 2012 legislation were found in green color tones and blue and white colors, respectively (Ministry of Health 2013).

Fluorescent, metallic and similar inks containing toxic metals in large proportions obviously expose individuals to environmental hazards. Spot colors are created with a pantone matching system (PMS). In many PMS colors, the presence of copper, barium, or both, and more than 40 metals in a single metal, constitutes a potential health risk (Zalewski 1994).

The appearance of the substrates of paper-based packages are developed with coating, dyeing, and printing processes. Contamination from the surface and printing ink colors of paper-based food packaging is a major source of toxic metals (EPA/310-R-02-002 2002). The identification of a large part of the characterization of the packages is determined by measuring the optical properties of the colors and brightness. The other part is formed by the percentage of ash and basis weight.

The chemical additive components of the processes used for improving the basic content and surface characteristics of the cardboard used in food packaging products cause risks for food safety, human health, and environmental pollution. An important group of components that cause toxicological effects among these components is toxic metals (Conti 1997; Conti and Botrè 1997; Leks-Stepien 2011; FSSAI 2016). The identification of toxic metals migrating from paper-based packages through food migration is crucial in ensuring the quality and safety of packaging and in assessing compliance with food legislation guidelines that potentially affect human health.

Within the scope of this aim, the characterization of some food packaging structures and the determination of toxic metals originating from both structure and migration have been interpreted for their compliance with food legislation. In addition, the relationship between the ash, weight and optical characteristics parameters describing the structural characterization of the package and toxic metals was interpreted and also tested with Pearson correlation relationship using SPSS 17.0 packet program.

EXPERIMENTAL

Materials

The samples were collected at Istanbul, Turkey, fast food restaurants and wrapped with stretch film for storage. Samples were paper, paperboard, corrugated board wrappers, and related food packaging. At least three specimens were collected in each sample. Samples were obtained by collecting unopened food packages from fast food chains and individual ready-made food restaurants and wrapping them with PE film stretch. Different types of papers that come into contact with food directly include paper, bag, and container-type packages. At least three specimens were collected for each type of test sample. The packages were manufactured of paper, cardboard, and corrugated cardboard base materials.

These are used as the main packaging materials, in addition to Al foil and polyethylene (PE) film side materials. The base materials are directly used individually or as laminated in combination with each other. The side materials are used together with the basic materials to enhance the appeal and the attractiveness of the packages in different functions. The packaging samples described are given in Table 1. In addition, characterization of packaging samples have been described according to their color (optic properties), grammage, and ash test.

Table 1. Description of the Analysed Packaging Samples

Paper Packaging		
1	Inner wrapping paper	White coated, low-grammage paper
2	Outer wrapping paper	Coated, white colour, printed thin paper
3	Wrapping paper 1	Coated brown paper
4	Wraping paper 2	Coated thin paper
5	Hamburger paper	White bleached printed thin paper
6	Paper bag	Brown kraft, low-grammage paper
7	Flour packaging	Outer layer white and printed, inner layer brown kraft paper
Paperboard Packaging		
8	French fries	Coated white paperboard
9	Pasta 1	Coated, dense dark colored, mat lacquered, printed
10	Pasta 2	Coated, dense dark colored, mat lacquered, printed
11	Cake	Grey, recycled printed box laminated from inside with white plastic film, upper surface laminated with dense colored, painted and bright lacquered paper PE film
12	Pita 1	Outer surface laminated with paper coated by PE film lacquered with recycled, yellow bright color, inner surfaces smooth and grey
Corrugated Board Packaging		
13	Lahmacun 1	Bottom surface and printed upper surface and laminated with imitation (recycled kraft test liner) carrier surface paper; one middle fluting layer
14	Lahmacun 2	Bottom surface and printed upper surface and laminated with imitation (recycled kraft test liner) carrier surface paper; one middle fluting layer
15	Pita 4	Corrugated board packaging with imitation kraft test liner carrier including recycled material and one middle floating layer
16	Pita 5	Imitation kraft test liner carrier including recycled material and one middle fluting layer
17	Pizza 1	Upper surface is laminated whitened and printed paper, imitation kraft test liner carrier including recycled material and one middle fluting layer
18	Pizza 2	Upper surface is laminated whitened and printed paper, imitation kraft test liner carrier including recycled material and one middle fluting layer

Methods

Charactarization of packaging

Dry matter, grammage, ash determination, and optical property tests according to C/2º light source were determined for characterization of packaging samples. The determination of toxic metal migration to the food due to the structure of the packaging was performed separately. Dry matter determination was performed according to the method specified in ISO 287 (2009) using a drying oven (Nüve FN 400, Istanbul, Turkey). Weight measurements were performed using a digital scale (Scaltec 31, Istanbul, Turkey). Other standards used included: standard climate conditions (ISO 187, 1990); grammage determinations (ISO 536 1998), ash content (ISO 1762 2015), and CIE whiteness (ISO 11476 2010).

The optical properties test was used to make the definitions color of packaging samples. Optical properties were measured using an Elrepho 070R (Istanbul, Turkey), using indoor light C/2º according to ISO 11476 2010. The standard tests were carried out according to C/2º light source; CIE whiteness, *L*, a*, b** (C/2°); TS ISO 5631-1 (2009); CIE whiteness, *L*, a*, b**, ISO 7724 (1984) (Zwinkels and Noel 2014); C/2º ISO brightness the ISO 3688 (1999); the yellowness (*Y*) index test the DIN 6167 (1980).

Toxic metal content

Instrumentation: The samples were digested using a microwave oven (Berghof, Istanbul, Turkey). The measurements were made using an inductively coupled plasma optical emission spectrometry ICP-OES device (Perkin Elmer Optima 7000 DV, Istanbul, Turkey) and ICP-MS (Thermo Scientific Series 2, Istanbul, Turkey) for measurements of Hg content.

Toxic metals for structural sources in packaging: Samples, whose basis weights and dry matter estimates were determined, were prepared for heavy metal analysis by manually tearing the samples with plastic gloves with 0.4 to 0.5 g dry weights. Samples were placed in Teflon tubes for structural toxic/heavy metal analysis and 5 mL of 5% nitric acid (HNO_3) and 2 mL of hydrogen peroxide (H_2O_2) were added. Digeston was performed in microwave oven (Berghof, Istanbul, Turkey) according to EPA Method 3052 (1996) given in Table 2 and by considering the microwave heating programs. The amounts of toxic metals in the prepared solutions were determined on the ICP-OES and ICP-MS instruments by filtering the solutions through blue band filter paper and completing them to 50 mL with ultrapure water.

Table 2. Procedure Used to Burn Microwave Samples

	Temperature (°C)	Pressure (Bar)	Ramp	Duration (Min)	Power (Watt)
1	120	35	5	2	90
2	140	35	10	5	90
3	170	35	10	15	90
4	50	35	1	1	0
5	50	35	1	1	0

Migration test

A migration test (M) was performed to determine the migration probability of toxic metals from paper based packages to food. As a sample for the migration test, specimens having a total surface area of 100 cm^2 were immersed in 100 mL of food simulant solution (3% w/v CH_3COOH) under acidic (pH 4.0) for 24 h at 40 ºC conditions (EN1186 European Committee for Standardization 2002). An aliquot of the simulant and blank was taken by ICP-OES, and ICP-MS was performed on the simulant and standard. All the migration measurements were made in duplicate. For determination of migration-originated toxic metals in paper-based packages, specimens with an area of 1 dm^2 were prepared by immersion in 3% acetic acid at 40 °C for 24 h. Toxic metal quantities of the solutions prepared were measured in ICP-OES and ICP-MS instruments.

The standard reference material (SRM) (1575, a trace elements in pine needles, *Pinus taeda*, Denver, CO, USA) prepared by NIST (National Institute of Standards and Technology) was used to compare the analysis method accurately. Table 3 shows device and certificate values of the ICP-OES used for toxic metal determination.

Table 3. ICP-OES and Certificate Values

	Device Values		Certificate Values	
	Mean ($mg.kg^{-1}$)	±Std	Mean ($mg.kg^{-1}$)	±Std
Pb	0.22	0.048	0.167	0.015
Hg	0.003259	0,008	0.003	0.008
Cd	0.213	0.0241	0.233	0.004
Ni	1.445	0.0585	1.47	0.1
Zn	36.0	0.217	38	2
Cu	2.672	0.0548	2.80	0.2
Al	551.7	3.34	580.0	30
Cr	0.398	0.013	0.3-0.5	

Table 4 shows limit values of solutions studied in the ICP-OES. The nitric acid + H_2O_2 and acetic acid solutions were used to prepare the samples as the solutions. The reagents acetic acid, HNO_3, and H_2O_2 were solutions obtained from Merck.

Table 4. Solutions limit values for LOD ($mg.kg^{-1}$)

Analyte	Linear regression coefficients	CH_3COOH 3% (w/v)	HNO_3+H_2O_2
Pb	0.9995	0.02	0.01
Hg	0.9999	0.0002-	0,005
Cd	0.9996	0.0053	0,0043
Zn	0.9999	0.2458	0.0373
Cr	0.9995	0.0066	0.0063
Ni	0.9995	0.0088	0.0069
Cu	0.9995	0.0262	0.0059
Al	0.9999	0.2236	0.2503

Table 5. Operating Conditions of ICP-OES and ICP-MS

ICP OES conventional nebulization	ICP MS for Hg	
Radio frequency	40 MHz	27 MHz
Forward power	1350 W	1400 W
Plasma gas flow rate	15.0 L min^{-1}	-
Auxiliary gas flow rate	0.2 L min^{-1}	0,80 L min^{-1}
Nebulizer pressure	120 kPa	Cool:13.0 L min^{-1}
Carrier gas flow rate	--------	Nebulizer Carrier gas:0.68 L min^{-1}
Nebulizer type	Concentric glass A	Nebulizer:Concentric glass
Spray chambre	cyclonic	Spray-Chamber:Cyclonic-------
Replicate read time	15 s	15 s
Number of replicates	3	4
Torch type	Quartz torch with a 2.0 mm I.D. alumina injector tube	Quartz Torch with 0.2 mm I.D. alumina injector tube
Sample flow rate	1.5 L min^{-1}	1.5 mL min^{-1}
$NaBH_4$ and HCl flow rate	--------	Extraction:202 V
$NaBH_4$ concentration	--------	0.3 % w/v
HCl concentration	--------	6 mol L^{-1}
Analytical lines conventional nebulization	Pb: 220.353 nm, Cd: 228.802 nm, Ni: 231.604 nm, Al:396.153 nm, Zn: 206.200 nm, Cu: 327.393 nm, Cr: 267.716 nm	Hg: 253.7 nm

Stock standard solutions

All standard metal solutions were supplied in packages of 100 mL with 1000 ppm concentration in ICP purity quality by the company HG Labs. Standard metal solutions prepared for calibration were prepared by using 10, 10, and 1 ppm mixed standard solutions that had been prepared in advance. Standard metal solutions prepared in five different concentrations (0.005 to 10 mg.kg^{-1}) for the calibration of the ICP-OES/MS device in mg.kg^{-1}.

Statistical Analysis

Microsoft Office (Excel-2003) was used for analysis and drawing charts. SPSS Statistics for Window Version 17.0 (SPSS Inc., Chicago, IL, USA) was used for the statistical analyses.

RESULTS AND DISCUSSION

Results of grammage, ash determination, and optical property for charactarization of packaging samples are given in Table 6.

Table 6. Characteristics of the Packaging

Samples	Gram. (gm^{-2})	Ash (%)	*L**	*a**	*b**	*W*	*T*	*F*	R_{457}	R_{457} *F*	Yellowness
Paper Packaging											
1	57	29.6	87.44	-2.75	9.29	30.33	-0.66	6.78	60.7	1.42	15.9
2	57	29.6	86.58	2.68	1.67	60.82	0.16	10.42	67.7	2.4	5.9
3	196.27	4.37	77.94	0.4	-2.19	83.5	0.25	1.14	59.3	0.1	1.1
4	58.5	28	85.1	-0.47	0.58	63.5	0.51	0.13	65.9	0.02	0.8
5	58.5	28	68.24	19.49	17.6	11.37	0.08	1.1	35.6	0.3	45.2
6	46.8	1.13	63.49	6.62	17.32	12.61	0.06	-0.48	25.5	-0.01	51.0
7	142.5	9.7	69.85	6.58	5.09	46.1	0.04	14.38	42.4	2.96	20.6
Average	88.1 ±57.8	18.6 ±13.0	77.0 ±9.8	4.7 ±7.4	7.1 ±8.0	44.1 ±27.3	0.07 ±0.36	4.78 ±4.8	51.0 ±16	1.0 ±1.2	20.1 ±20.6
Paperboard Packaging											
8	620	12.34	82.91	1.97	1.42	58.53	0	15.09	64.36	3.73	17.38
9	285.7	10.47	70.69	3,19	18.24	16.43	0	1.42	36.96	0.07	46.55
10	322.6	9.58	55.02	0.84	-8.73	51.85	0	3.08	36.1	0.2	7.29
11	426	12.14	63.31	8.28	-0.2	49.44	9.22	5.28	37.38	-0.03	47.79
12	587	21.97	70.4	5.24	13.54	13.57	-0.31	7.12	34.53	1.11	37.61
Average	448.3±151.2	13.3±5	68.5±10.3	3.9±2.9	4.9±10.9	38±21.3	1.8±4.2	6.4±5.3	41.9±12.6	1±1.6	68.5 ±10.3
Corrugated Board Packaging											
13	288.71	11.29	64.29	3.92	13.09	14.43	0.02	4.87	28.17	0.83	38.29
14	320.9	10.88	59.31	44.77	19.54	0	0	14	16.65	0.1	58.2
15	327	10.7	58.62	7.02	20.1	0	0	1.12	15.97	0.07	58.37
16	399.2	10.88	58.29	22.59	16.11	42.85	0	27.28	28.07	0.75	54.55
17	413	10.85	41.91	3.98	9.65	30.64	0	2.88	9.71	0.11	38.28
18	375.1	9.65	64.56	0.66	3.01	26.09	0.33	2.27	35.58	0.38	18.39
Average	354±49.1	10.7±0.6	57.8±8.3	13.8±17	13.6±6.5	19±17.3	-0.05.8±0.14	8.7±10.2	22.4±9.7	0.37±0.34	31.3 ±18.1

Gram:Grammage

Characteristics of the Packaging

Grammage values

Grammage values of paperboard and corrugated board package samples distributed homogeneously and closely to each other. Distribution of paperdboard packaging varied with different grammage values heterogeneously (Table 6).

Content of ash

It has been found that there is less than 1.15% ash in unprinted pulp, about 1.49% in inkless and printed pulp, and higher than 16.5% in paper with mineral or other chemical additives (İmamoğlu 2001). Ash content in paper packaging ranged from 1.13% and 29.6%. Ash content in paperboard packaging was between 9.58% and 21.97% (Table 6). It was observed that the ash content of paper packaging was higher than of paperboard packaging, which was likely due to filling and surface processes. Ash content of corrugated board packaging was between 9.65% and 11.29%, which was lower than the ash content of low grammage paper packaging. The change between 1.13% and 29.6% of all packages reflects that the paper packages are within the ash range.

Optical Characteristics

The optical properties used in the characterization of paper-based packaging samples were measured according to C/2º (interior) light source.

C/2º *L*, a* and b* values in packaging*

In all packaging, *L** values indicated a mostly white color and distribution. It was found that paperboard packages ranked higher than the paperboard and corrugated board packagings, with the highest *L** values with the minimum and maximum level and bright white colors. Paperboard packaging ranked as the second and corrugated board packaging ranked as the third. The dyeing process was applied to surface-treated paperboard and paperboard packaging and to the corrugated board packaging which were not surface-treated. It was found with *CIE a* values* that green tones were mostly dominant in paperboard and corrugated board packaging and red tones were seen in a very small portion whereas red tones were all dominant in paperboard packaging.

The *b** values in the all packaging revealed that generally yellowish tones were observed and a few blue tones also were apparent. It can be said that the color distribution of paper packaging was different than both paperboard and corrugated board packaging. The C/2º *CIE W, T:* CIE *W* and *T* values describe fluorescent whitening components. CIE *W* and *T* values showed that white and green tones were dominant in paperboard packaging while white and red tones were dominant in cardboard and corrugated board packaging (Table 6).

F and R_{457} and R_{457} F brightness values in packaging: The fluoresent (F) colors were highest in paper packaging, second row in corrugated board, and the last row in cardboard packaging. It has been determined that R_{457} brightness values have significantly higher than R_{457} F brightness values. Paper packaging having a low yellowness value showed a heterogeneous distribution, whereas packaging with a high yellowness value had a homogeneous distribution.

Toxic Metals in Packaging

Paper, paperboard, and corrugated board packaging are used in several areas; they are present in a very large portion of food packaging. In legislation related to food packaging that is in direct contact with food, production of food packaging using primary fibers is considered. On the other hand, in recycled paper-paperboards, the content of recycled fibers has reached 80% (Conti and Botrè 1997). In recycled paper and paperboard packaging applications for packages that are indirect contact with the food, contaminations and impurities, which are absorbed by the structural components of recycled materials and manifested later on the food, are determined to a large extent in order to increase the safety and raise awareness of consumers (Triantafyllou *et al.* 2007).

According to an EU directive (EC 94/62 2012), virgin and recycled paper or paperboard sub-products used in packaging have limits regarding toxic metals, including Pb, Cd, Hg, and Cr due to color and ink residues from waste. Specifically, the directive states that the amount of these metals should not exceed 100 mg per 1 kg of packaging material. The migration of packaging structural components into food should not exceed 100 ppm in grammage over the course of five years. Sources of toxic metals in paper, paperboard and corrugated board packaging include (EC 94/62 2012):

- Toxic metals, in general, arise from chemical substances and additives used in the production process, and also from corrosion of machines and equipment (Eroğlu 2004).
- Paper packaging and tatto uses a wide range of colors. It commonly includes contaminants such as toxic metals. Certain greens contain Pb, Cr, and soluble Cu metal. Reds may contain Pb and Cd, yellows contain Cd and Zn, and blues contain Co and Cu. Whites contain Cd, Pb and Zn, while blacks contain Cd and Pb (EPA 2009; Ministry of Health 2013).
- Fluorescent whitening agents, solutions- based, are widely used in office paper products and packaging products.

Table 7. Toxic Metals from Structural Sources in Packaging (mg.kg^{-1})

Sample	Pb	Hg	Cd	Zn	Ni	Cu	Cr	Al
1	9.13	n.d	0.06	7.62	1.97	17.31	2.75	11.47
2	9.13	n.d	0.06	7.62	1.97	17.31	2.75	11.47
3	1.46	0.39	0.04	3.06	1.37	2.80	0.51	34.77
4	12.94	0.51	0.03	10.11	1.03	0.52	1.48	3,632
5	4.50	0.09	0.12	4.03	1.42	3.62	1.69	1,327
6	1.39	0.86	0.18	5.89	1.14	0.62	0.91	276.80
7	1.46	1.82	0.04	9.66	3.28	13.71	2.44	5,431
8	2.51	0.01	0.02	3.44	1.21	0.92	2.02	2,670
9	1.45	0.35	0.02	1.38	1.21	49.71	0.93	1,546
10	1.99	0.56	0.06	1.36	0.92	24.89	1.09	1,394
11	3.83	0.34	0.02	15.63	2.11	31.24	1.80	3,683
12	11.06	0.99	0.09	17.33	2.50	32.13	2.74	5,642
13	12.77	n.d	0.16	40.94	3.28	0.00	6.14	2,466
14	6.61	1.20	0.13	37.75	4.73	30.33	4.55	3,523
15	7.97	2.45	0.13	61.30	4.38	27.14	6.16	3,295
16	1.69	0.87	0.07	13.98	2.45	7.57	1.38	1,268
17	3.90	3.80	0.09	21.81	4.19	17.52	2.88	3,500
18	4.25	2.13	0.09	22.46	4.93	166.60	3.60	3,909

Furthermore, the US has enacted legislation and regulations that banned the sale or distribution of packaging sub-material containing cadmium, lead, mercury, or hexavalent chromium. According to The Toxics in Packaging Clearinghouse (TPCH), the total concentration of the metals in the product shall not exceed 100 ppm in four years. As distinct from the food legislations and regulations of other countries, most other US states have enacted regulations that prohibit or restrict the addition of lead, cadmium, mercury, or hexavalent chromium intentionally in ink, dye, pigment, adhesive, stabilizer and other packaging components (EPA 2009; Ministryof Health 2013).

Toxic metal values, sourced from paper, paperboard, and corrugated board packaging structures and migrated from packaging through the process are given in Tables 7 and 8.

Table 8. Migration of Toxic Metals in Paper Packaging (mg.kg^{-1})

Sample	Pb-M	Hg-M	Cd-M	Zn-M	Ni-M	Cu-M	Cr-M	Al-M
1	1.05	n.d	0.02	0.71	0.30	0.99	0.35	31.53
2	1.05	n.d	0.02	0.71	0.30	0.99	0.35	31.53
3	n.d	n.d	0.00	n.d	n.d	n.d	0.03	1.45
4	n.d	n.d	n.d	n.d	n.d	n.d	0.07	1.15
5	9.42	n.d	n.d	n.d	n.d	n.d	0.41	1,022
6	0.10	n.d	0.28	67.15	3.08	0.86	0.37	223.60
7	2.06	n.d	0.08	33.52	1.26	5.73	0.68	651.70
8	0.01	n.d	n.d	n.d	0.28	0.22	0.45	310.10
9	n.d	n.d	0.03	n.d	1.10	0.03	0.04	1,218
10	0.20	n.d	1.98	n.d	0.30	1.26	0.51	1,175
11	6.39	n.d	15.68	307.10	16.72	14.01	4.28	173
12	2.25	n.d	0.18	31.61	0.94	3.83	0.51	542.40
13	n.d	n.d	n.d	n.d	n.d	n.d	n.d	935.70
14	1.05	n.d	0.16	39.45	3.08	5.94	1.52	966.90
15	4.79	n.d	0.53	82.62	2.75	5.89	3.71	1,046
16	7.96	n.d	1.89	59.57	3.39	4.39	1.80	932.10
17	5.28	n.d	0.72	30.87	1.47	1.17	0.51	996.40
18	1.05	n.d	0.38	25.62	4.18	1.24	0.77	813.70

n.d.: None detected

Pb Concentration in Packaging

Structural Pb concentration in packaging

In paper packaging the Pb concentration was between 1.39 and 12.9 mg.kg^{-1} (Table 7). Wrapping papers were the most remarkable, with high values in paper packaging with very different Pb distributions. In wrapping papers, L^* a^*, b^*, and CIE W and CIE T color values were high, and it was thought that pigments and paint components used in coating and similar coloring processes to obtain these color values are the reason of high Pb heavy metal values (Zalewski 1994; Kim *et al.* 2008). The high content of ash, despite lower grammage in paper packaging, supports this explanation (Table 6). In paperboard packaging the Pb concentration was between 1.45 and 11.1 mg.kg^{-1}. Corrugated board packaging, between 1.69 and 12.77 mg.kg^{-1} had high Pb concentrations (Table 7). Seven out of 18 packaging values were below the specified limits (3 $mg.kg^{-1}$; Council of Europe 2002; The European paper and board food packaging chain 2012).

Some of the cardboard packaging samples, with the dominant red color which their high L^* and a^* values showed, can be said to be the source of Pb toxic metal. In addition, the colors *W* (white), *T* (red), and Y (yellow) values showed in corrugated board packaging can be source of Pb in high level (Table 6).

When examining the distribution of Pb amounts of all packaging within each group of packaging, it was observed that values of paperboard and corrugated board packaging were distributed homogenously and in close intervals for both groups, whereas paper samples demonstrated a very heterogeneous distribution.

According to Pearson correlation analysis, there was a strong positive linear correlation between the Pb concentration of the packaging and the ash variability (p <0.01). The importance of ash content was supported by L^*, a^*, b^*, CIE *W* values ($p < 0.05$), and also by R_{457} brightness and yellowness values ($p < 0.01$)

It was found that average Pb amounts in packaging were substantially lower than the related limit value specified in the Turkish Food Codex (20 $mg.kg^{-1}$ for the egg viols). They were also found to be substantially lower than values specified in some other research (0.28 to 0.99 g. g^{-1}) (Skrzydlewska *et al*.2003)

Pb concentration sourced from contact of packaging with food

The amount of Pb ranged from n.d. (none detective) to 9.42 $mg.kg^{-1}$ in paper packaging, n.d to 6.39 $mg.kg^{-1}$ in paperboard packaging, and n.d. to 7.95 $mg.kg^{-1}$ in corrugated board packaging (Table 7). According to Conti and Botrè (1997), Pb limit values (0.01 $mg.kg^{-1}$), for eight samples in food migration did not exceed from a total of 18 samples, five samples of paper packages, two samples of paperboard packaging, and an sample of corrugated board packages.

According to the Pearson correlation analysis, Pb migration concentration of the packaging was found to have a positive linear correlation with strongly yellowness variable (p <0.01) and with moderate a^* variable (p <0.05).

It can be said that the paper packaging that did not involve a coating process but included low-weight primary fiber did not exceed the Pb limit values and that the secondary fiber-containing packages and color residues of the printing inks are toxic metal sources (Table 1).

It was determined that the Pb concentration was similar to the literature studies conducted (Castle *et al.* 1997; Conti *et al.* 2007; Duran *et al.* 2013). In the studies conducted on migration of the packaging, Tiggelman (2012) stated the necessity for a test of humid and fatty food in direct contact with food packages against ink contamination. Conti *et al.* (1996) also reported that the lack good quality waste can result in 50% of the recycled fiber-containing packagins produced from different waste-based paper sources exceeding limit values in Pb migration (with 7 of the 14 samples).

According to the World Health Organization (WHO) Joint Expert Committee for Food Additivies (JECFA),the provisional tolerable weekly intake (PTWI) of Pb is 0.025 mg per unit (kg)body weight (Conti 1997).

Hg Concentration in Packaging

Structural Hg concentration in packaging

The amount of Hg ranged from n.d. to 1.82 $mg.kg^{-1}$ in paper packaging, 0.01 to 0.99

mg.kg^{-1} in paperboard packaging, and n.d. to 3.8 mg.kg^{-1} in corrugated board packaging. The high Hg levels in corrugated board packaging were thought to be due to the use of Hg compounds in order to increase the surface energy of the paper (Scott 1996; Table 1). Among all packaging, paperboard packaging demonstrated lower amounts of Hg, and that the higher amounts belonged to corrugated board, with a value of 3.80 mg.kg^{-1} (Tables 1 and 6). A Pearson correlation analysis, among the Hg concentration of the packaging and the L^* and R_{457} brightness variables, showed a strong negative linear correlation ($p < 0.01$).

The highest amount of Hg permitted in paper/paperboard structure, for paper and paperboard materials and products that are in direct contact with food, is 0.3 mg.kg^{-1} (The European paper and board food packaging chain 2012). It was found that Hg levels in the structural content of paperboard and corrugated board packaging mostly exceeded this limit value, whereas only five out of 18 samples among packaging were below this limit value.

In this respect, the Hg contents of the paper, paperboard, and corrugated paperboard packaging usually exceeded the limit values for this structural component: only in three samples of paper packaging and two samples of paperboard and one sample of corrugated paperboard, did the Hg contents remain below the limit value (Tables 1 and 6).

Migration Hg values via contact of packaging with food

Although the limit value for structural Hg content determined by international food legislation was exceeded in some samples, no Hg amounts due to migration *via* direct contact with the food was determined in any of the paper, paperboard, and corrugated board samples (Table 7).

Cd Concentration in Packaging

Structural Cd concentration in packaging

The colors red and yellow, which are commonly used among the bright colors used in fine arts, can be obtained using Cd. The demand for these colors is also very high in print inks, but there are also high quality alternative pigments (Zalewski 1994).

The amount of Cd ranged from 0.03 to 0.18 mg.kg^{-1} in paper packaging, 0.02 to 0.09 mg.kg^{-1} in paperboard packaging, and 0.07 to 0.16 mg.kg^{-1} in corrugated board packaging.

Cd concentration was found to have positive linear correlation with optical characteristics. The correlation was strong with b^* ($p < 0.01$) and a moderate ($p < 0.05$) was obtained relative to yellowness. In addition, decrease in Cd concentration was found to have a strong correlation with high values with L^*, CIE W, R_{457} brightness variables.

It was found that values did not exceed the Cd limit value (0.5 mg.kg^{-1}) with respect to The European paper and board food packaging chain 2012. This may be related to the sources that are used in paperboards for red, a^*, and Y color (Table 6).

In paperboards, the high C/2º CIE T values for some paperboard support this view (Zalewski 1994) (Table 6). This difference was attributed to the wide range of quality of paints and pigments. The sample values were below the values obtained in other literature surveys (Conti 1997; Skrzydlewska *et al.* 2003; Duran *et al.* 2013).

Migration Cd values via contact of packaging with food

Results of migration tests for the 18 samples of paper, paperboard, and corrugated board food packages ranged from n.d. to 0.28 mg.kg^{-1}, n.d. to 15.68 mg.kg^{-1}, and n.d. to 1.89 mg.kg^{-1}, respectively. Also, values of Cd in all packages ranged from 0.02 to 0.18

$mg.kg^{-1}$.

Levels did not exceed the migration Cd limit value (Conti and Botrè 1997; 0.005) in paper packaging, except for in two samples (Table 7). It was observed that levels did not exceed the migration Cd limit value determined by European Commission (2015), with the exceptions of one sample within paperboard groups and two samples within corrugated board group (Table 7).

In all packaging, the amount of migration of Cd was measured to be between n.d and 15.68 $mg.kg^{-1}$. It was observed that paper and corrugated board packaging were distributed homogeneously within close intervals, whereas paperboard packaging displayed a heterogeneous distribution. The amounts exceeded the limit values by European Commission in all but two samples (Table 6). According to CoE (1992), in the amounts of food contact-originated migration of packages, eight samples among all packages had been observed to have exceeded the limit value (Castle *et al*. 1997; European Commission 94/62 2012). Although the amount of Cd from the structured origin of the packagings does not exceed the limit values, most of the paperboard and corrugated board packaging originating from migration had been found to have exceeded the limit values. Based on Pearson correlation analysis, the Cd migration variable had a very strong positive linear correlation with CIE *T* ($p < 0.01$).

Although structural Cd amounts of packaging did not exceed the limit values, most of the migration-related paper packaging values were very low. It can be argued that this might depend on the low grammages and very low or lack of recycle fiber content. For paperboard and corrugated paperboards, on the other hand, the high values may have been caused by dissolution during acetic acid extraction for migration, given the increase in grammage and recycled fiber content, as well as the low quality colorants used (Table 7).

Zn Concentration in Packaging

Structural Zn concentration in packaging

Paper occasionally is filled with zinc oxide or zinc sulphate compounds, which are used to increase opacity and for the production of copy and packaging papers (Erkan and Malayoğlu 2001). Zn is also used in fine arts and can be increased when white color pigments are employed to obtain good light tones of other colors, and to apply metallic colors (Zalewski 1994).

The high L^* and W value supported the relationship with Zn (Table 6). The Zn values of paper packaging were 3.06 to 10.11 $mg.kg^{-1}$, for paperboard packaging they were 1.36 to 7.33 $mg.kg^{-1}$, and corrugated board packaging had 13.98 to 61.30 $mg.kg^{-1}$ (Table 7). According to EPA 2012 legislation, Zn amounts of paper-based food packagings did not exceed max limit value (50 $mg.kg^{-1}$) except for one of corrugated board specimens. According to Pearson correlation analysis, the Zn content from packaging had a very strong negative linear correlation with CIE W ($p < 0.05$) and with R_{457} brightness the correlation was strong ($p < 0.01$).

Migration Zn values via contact of packaging with food

In paper, paperboard and corrugated packaging, Zn migration values ranged from n.d. to 67.15 $mg.kg^{-1}$, n.d. to 307.10 $mg.kg^{-1}$, and n.d. to 82.62 $mg.kg^{-1}$, respectively (Table 7). It was observed that values from all packages demonstrated a homogeneous distribution ranging between n.d. and 307.1 $mg.kg^{-1}$ (Table 7). According to Pearson correlation analysis, the concentration of Zn migration had a very strong positive linear correlated with

CIE *T* ($p < 0.01$). Zn amounts from packaging were substantially higher than the amounts sourced from direct contact with food. This was similar to literature findings (Castle *et al.* 1997).

Ni Concentration in Packaging

Structural Ni concentration in packaging

The results for Ni in paper, paperboard, and corrugated board packaging ranged from 1.03 to 3.28 $mg.kg^{-1}$, 0.92 to 2.50 $mg.kg^{-1}$, and 2.45 to 4.93 $mg.kg^{-1}$, respectively. (Table 6). According to Pearson correlation analysis, Ni content values were found to have a moderate negative correlation with L^*, CIE *W* and R457 brigthness ($p < 0.05$).

Migration Ni values via contact of packaging with food

The results of Ni for paper, paperboard and corrugated board packaging were n.d.-3.08 $mg.kg^{-1}$, 0.28-16.72 $mg.kg^{-1}$, and n.d.-4.18 $mg.kg^{-1}$, respectively (Table 7). Pearson correlation analysis showed that Ni migration values had a very strong positive linear correlation ($p < 0.01$) with CIE *T*.

Increased Ni levels were attributed to the green pigments and inks included in waste paper sources when recycled paper production is as raw material, and also to the use of green color components in colorizations of recycled new paper products (Mertoğlu-Elmas, 2017 and Table 6). As the daily intake limit of Ni, according to FAO/WHO (1994), is 100-300µg, the Ni levels in packaging samples did not represent a source of health risk. It was found that these values were below the values obtained in some published studies (Castle *et al*. 1997; Conti 1997; Duran *et al.* 2013).

Cu Concentrations in Packaging

Structural Cu metal concentrations in packaging

The results of Cu for paper, paperboard, and corrugated board packaging were 0.52 to 17.31 $mg.kg^{-1}$, 0.92 to 49.71 $mg.kg^{-1}$, and n.d. to 166.6 $mg.kg^{-1}$, respectively (Table 6).

Migration Cu values via contact of packaging with food

Data obtained from migration tests for paper, paperboard, and corrugated board food packaging ranged from n. d. to 5.73 $mg.kg^{-1}$, 0.03 to 14.01 $mg.kg^{-1}$, and n. d. to 5.94 $mg.kg^{-1}$, respectively (Table 7). Cu metal was mostly observed in blue color (Tables 6; Mertoglu-Elmas 2017). According to Pearson correlation analysis, Cu migration was found to have a strong positive correlation with CIE *T* ($p < 0.01$).

According to EPA guidelines, the amount of Cu paper based packaging did not exceed (25 $mg.kg^{-1}$). Also, for an adult, the recommended maximum daily amount of Cu intake is 3 mg (FAO/WHO, 1999). The migration of Cu metal from packaging did not create a health risk by the FAO/WHO (1999) (Conti 2007; Duran *et al.* 2013). Also, structural Cu levels in packaging were mostly below the limit values, except corrugated board sample (166 $mg.kg^{-1}$) which was related to the dense use of blue colors.

Cr Concentrations in Packaging

Structural Cr metal concentrations in packaging

The results of Cr for paper, paperboard, and corrugated board packaging were 0.51 to 2.75 $mg.kg^{-1}$, 0.93 to 2.74 $mg.kg^{-1}$, and 1.38 to 6.16 $mg.kg^{-1}$, respectively (Table 6). These amounts were below the values obtained by Skrzydlewska *et al.* (2003) (0.25 to 0.64

$mg.kg^{-1}$). Pearson correlation analysis showed Cr content values were to have a moderate negative correlation with CIE W ($p < 0.05$).

Migration Cr values via contact of packaging with food

Data from migration tests for paper, paperboard and corrugated board food packaging range from 0.03 to 0.68 $mg.kg^{-1}$, 0.04 to 4.28 $mg.kg^{-1}$, and n.d to 3.71 $mg.kg^{-1}$, respectively (Table 7).

The daily intake of Cr ranged between 50 and 200 mg (WHO 1996; Bratakos and Lazos 2002). The values of structural Cr and Cr from migration were below the limit values defined by EC (3.05 $\mu g.dm^{-2}$) (Duran *et al.* 2013; Resolution AP, Council of Europe 2015). Based on Pearson correlation analysis, Cr migration was strongly and linearly correlated with CIE T ($p < 0.01$) and with the yellowness variable in the moderate level ($p < 0.05$).

Al Concentrations in Packaging

Structural Al metal concentrations in packaging

Aluminum in packaging arises from aluminium sulphate, aluminium chloride hydroxide, aluminium formiate, aluminium nitrate and sodium aluminium components used as precipitators, stabilizers, and paper production chemicals that are used for improving all product and surface characteristics of paper and paperboard BfR (2017). According to Pearson correlation analysis, Al content values were positively and linearly correlated with ash in the strong level ($p < 0.01$) and with L^* in moderate level ($p < 0.05$) .

Structural Al metal concentrations in packaging

The results of Al analysis in paper, paperboard, and corrugated board packaging, were 34.8 to 11,470 $mg.kg^{-1}$, 1.394 to 5,642 $mg.kg^{-1}$, and 1.268 to 3,909 $mg.kg^{-1}$, respectively(Table 8). Pearson correlation analysis showed the Al content to have a strongly positive correlation with ash ($p < 0.05$), and it was moderately correlated with L^*, R_{457} brightness and R_{457} F fluorescent brightness ($p < 0.05$) in the positive direction.

Migration Al values via contact of packaging with food

Data from migration tests for paper, paperboard, and corrugated board food packaging ranged from 1.15 to 1,022 $mg.kg^{-1}$, 1.73 to 1,218 $mg.kg^{-1}$, and 813.7 to 1,046 $mg.kg^{-1}$, respectively (Table 9). Pearson correlation analysis of Al migration revealed a negative linear correlation with L^* strong ($p<0,01$), CIE Wmoderate ($p<0,05$) and R_{457} brightness strong ($p < 0.01$). In addition, it was found to have a moderate positive linear correlation with yellowness variable ($p < 0.05$).

According to EN 13428 (2004) environmental management standard, wastes of paper based packaging include toxic metals of emission, ash, or leaching which emerge as a result of burning. Similar processes in the reduction of the concentration to the lowest levels is reported. The hazard wastes such as emission, ash, or leak generated from known heavy metal concentration packaging wastes of the disposal, can be reduced to the lowest levels. Thus, it will have contributed to environmental protection management

CONCLUSIONS

1. In virgin and unbleached paper packaging, Pb amounts were below food legislation

limit values; whereas in white coated bleached kraft inner papers, recycled paperboard and corrugated board packagings, Pb amounts exceeded limit values.

2. Despite the fact that, in the majority of packages, structural Hg amounts were above limit values, Hg was not found in the migration from packaging.
3. Though the amount of Cd in packaging structure did not exceed limit values, most of the migration-related paper packaging values exceeded the limit values. This may have been caused by dissolution of low quality colorants during acetic acid extraction for migration.
4. It can be said that structural Zn amounts of packaging were substantially higher than the amounts sourced from migration.
5. In recycled corrugated packaging, green inks and paints have become a source of increasing Ni.
6. In paperboard and corrugated board packaging, the high Cu content is due to high density blue color.
7. Cr levels resulting from structural of corrugated board packaging were high than paper and paperboard packaging due to recycled
8. The amount of Al resulting from the migration of packagins are 10 times lower than the structural ones.
9. Color pigments and dyes have turquoise, yellow and white toxic metal sources, mainly red color in from light to dark color scale. The existence of these colors determined with the optical characteristics of paper, paperboard, and corrugated board packaging with respect to two different sources of light. Toxic metals can be said to dominate mainly color pigments such as green for Ni,.white for Zn and Pb and red and blue for Cu metals.
10. Applying coloring/dyeing process with dyes dissolving in water and acidic platform to corrugated board packaging without surface treatment can be said to result in increase in toxic metals.
11. According to EN 13428 (2004) the hazard wastes such as emission, ash or leak generated from known heavy metal concentration packaging wastes of the disposal, can be reduced to lowest levels and the environmental management can be also provided indirectly. With this study, it will be possible to control the compliance of toxic metals in paper-based food packages with the food legislation and to minimize the leaks of toxic metals emerging as a result of processes such as packaging waste incineration according to EN 13428 (2004) and to prevent the deposition of these as emissions, ashes and wastes on soil ,as an indirect contribution to environmental management.

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REFERENCES CITED

Aksoy, B., Joyce, M. K., and Fleming, P. D. (2003). "Comparative study of brightness/ whiteness using various analytical methods on coated papers containing colorants," in: *TAPPI Spring Technical Conference and Exhibit*, Chicago, IL, USA, pp. 371-385.

BfR (2016). "XXXVI Paper and board for food contact," Federal Institute for Risk Assessment, (www.bfr.bund.de/en/thegerman_federal_institute_for_ risk_assessment__bfr_-572.html), accessed 01 July 2017.

Binderup, M. L., Petersan, G. A., Vinggaad, A. M., Rasmussen, E. S., Rosenquist, H., and Cederberg, T. (2010). "Toxicity testing and chemical analyses of recycled paper for food contact," *Food Add. and Cont.* 19(1), 13-28. DOI: 10.1080/02652030110089878

Bostancı, S. (1987). *Production Pulp and Technology*, Karadeniz Tecnical University Publishing, Trabzon, Turkey.

Bratakos, M. S., and Lazos, E. S. (2002). "Chromium content of selected Greek foods," *Science of the Total Environment* 290(1-3), 47-58. DOI: 10.1016/S0048-9697(01)01057-9

Caner, E., Farnood, R. , and Yan, N. (2006). "Effect of the coating formulation on the gloss properties of coated papers," in: *International Printing and Graphic Arts Conference*, Cincinnati, OH, USA.

Castle, L., Offent, C.P., Baxter, M. J. and Gilbert J. (1997). "Migrations studies from paperboard food packaging, 1. Compositional analysis," *Food Add. and Cont*, 14(1), 35-44.

Castle, L. (2014). *Systematic Derivation of Correction Factors (CFs) to Relate Chemical Migration Levels from Paper and Board into Foods, with the Migration or Extraction Values obtained using Food Simulants or Solvents*, The Food and Environment Research Agency, York, UK, (http://www.cepi.org/system/files/public/documents/publications/foodcontact/2015/CEPI%20correction%20factors.pdf).

Conti, M. E., Boccacci Mariani, M., Milana, M. R., and Gramiccioni, L. (1996). "Heavy metals and optical whitenings as quality parameters of recycled paper for food packaging," *J. Food Process. Preservation* 20(1), 1-11. DOI: 10.1111/j.1745-4549.1996.tb00336.x

Conti, M. E. (1997). "The content of heavy metals in food packaging paper boards: An atomic absorption spectroscopy investigation," *Food Research International* 30(5), 343-348. DOI: 10.1016/S0963-9969(97)00062-8

Conti, M. E, and Botrè, F. (1997). "The content of heavy metals in food packaging paper: an atomic absorption spectroscopy investigation," *Food Control* 8(3), 131-136. DOI: 10.1016/S0956-7135(97)00004-2

Conti, M. E. (2007). "Chapter 9. Heavy metals in food packagings," in: *Mineral Components in Food*, J. Nriagu and P. Szefer (eds.), CRC Press, Boca Raton, FL, USA, pp. 339-362.

Conti, M. E. (2008). "Heavy metals in food packagings, The state of the art," in: *Intergovernmental Forum on Chemical Safety*, Dakar, Senegal, (http://www.who.int/ifcs/documents/forums/forum6/roomdoc_hmfood.pdf)

Coppel, L. G. (2010). *Whiteness and Fluorescence in Paper Perception and Optical Modelling*, Licentiate Thesis, Mid Sweden University, Sundsvall, Sweden.

DIN 6167 (1980). "Description of yellowness of near-white or near-colorless materials," German Institute for Standardization, Berlin, Germany.

Duran, A., Tuzen, M., and Soylak, M. (2013). "Evaluations of metal concentrations in food packaging materials: Relation to human health," *Atomic Spectroskopy* 34(3), 99-103.

EN 13428 (2004). "Packaging- Requirements specific to manufacturing and composition – Prevention by source reduction," European Committee for Standardization, Brussels, Belgium.

EPA Digestion Method 3052 SW-846 (1996). Environmental Protection Agency, US.

EPA/310-R-02-002 Industry Sector Notebook Project (2002). *Pulp and Paper Profile of the Pulp and Paper Industry*, 2nd Edition, Environmental Protection Agency, Office of Compliance Office of Enforcement and Compliance Assurance Washington, DC, U.S.

EPA X9-97160301-0 the Northeast Recycling. (2009). *The Toxics in Packaging Clearing House (TPCH): An Assessment of Heavy Metals in packaging*, Environmental Protection Agency US. www.packaginglaw.com/special-focus/packaging-and-environmental-legislation-united-states-overview. (Accessed 06, 29, 2018)

Erkan, Z. E., and Malayoğlu, U. (2001). "Industrial raw materials and their properties used in the paper- paperboard industry," in: *Industrial Raw Materials Symposium*, Izmir,Turkey, pp. 250-257.

European Committee for Standardization. (2002). EN 1186-1: materials and articles in contact with foodstuffs. Plastics.Part 1: guide to the selection of conditions and test methods for overall migration. Brussels: European Committee for Standardization.

The European paper and board food packaging chain. (2012). *Industry Guideline for the Compliance Paper and Board Materials and Articles for Food Contact* (Issue No. 2), Confederation of European Paper Industries, Brussels, Belgium.

European Commission (EC) Regulation 94/62 (2012). "Packaging and packaging waste," European Union, Brussels, Belgium.

European Parliament and Council, 2015, *Commission Regulation (EU) No 94/62 Packaging and Packaging Waste*, European Comission, European Union, Brussels, Belgium.

FAO (1999). "The state for of food insecurity in the world," (www.fao.org/NEWS/1999/img/SOFI99-e.pdf), accessed 16 April 2018.

FSSAI (2016). "Study on the chemical contamination of pre-packaged food (retail) through packaging material," Revised Project Proposal (Amendment 2). Indian Institute of packaging, Bhawan, Near Bal Bhavan, Kotla Road, New Delhi, India.

JOINT FAO/WHO (1994). "Joint FAO/WHO foods standards programme," Report of the Ninth Session of the Codex Commıttee on Cereals, Pulses and Legumes, Via delleTerme di Caracalla, 00100 Rome, Italy.

Heikkla, P., and Rajala, P. (2000). "Drying of paper coatings equipment," in: *Textbook of Pigment Coating and Surface Sizing of Paper*, J. Gullichsen and H. Paulapuro (ed.), Gummerus Printing, Jyväskylä, Finland , pp. 543-546.

Hubbe, M. A., Pawlak, J. J., and Koukoulas, A. A. (2008), "Paper's appearance: A review," *BioResources* 3(2), 627-665.

ISO 187 (1990). "Standard atmosphere for conditioning and testing and procedure for monitoring the atmosphere and conditioning of samples," International Organization for Standardization, Geneva, Switzerland.

ISO 536 (1998). "Paper and board – Determination of grammage," International Organization for Standardization, Geneva, Switzerland.
ISO 1762 (2015). "Determination of residue (ash) on ignition at 525 degrees C," International Organization for Standardization, Geneva, Switzerland.
ISO 11476 (2010). "Paper and board – Determination of CIE whiteness, C/2° (indoor illumination conditions)," International Organization for Standardization, Geneva, Switzerland.
ISO 3688 (1999). "Preparation of laboratory sheets for the measurement of diffuse blue reflectance factor (ISO brightness)," International Organization for Standardization, Geneva, Switzerland.
ISO 5631-1 (2009). "Paper and board – Determination of colour by diffuse reflectance – Part 1: Indoor daylight conditions (C/2 degrees)," International Organization for Standardization, Geneva, Switzerland.
ISO 7724 (1984). "Paints and varnish – Colometry. Part 2: Color measurement," International Organization for Standardization, Geneva, Switzerland.
İmamoğlu, S. (2001). "Investigation of the flotation deinkability printed waste office paper," *Review of the faculty of Forestry, University of İstanbul,* A series 51(2), 81-89.
Kim, K. C., Park, Y. B., Lee, M. J., Kim, J. B., Huh, J. W., Kim, D. H., Lee, J. B., and Kim, J. C. (2008). "Levels of heavy metals in candy packages and candies likely to be consumed by small children," *Food Research International* 41, 411-418.
Kim, E. H., Lee J. Y., Kim C. H., and Park, T. U. (2017). "Effect of carriers chemicals on the optical properties surface-sized with fluorescent whitening agents," *BioResources* 12(2), 2982-2990. DOI: 10.15376/biores.12.2.2982-2990
Leks-Stepien, J. (2011). "Paper packaging materials and food safety," *Int. Circ. Educ. Inst. Graph Arts Technol. Manag.* 4, 49-51.
Martin-Dias, A. (ed.) (1994). *Innovative Clean Technologies Case Studies, Second Year Project Report* (EPA/600/SR-94/169), U. S. Environmental Protection Agency, Washington, D. C. US.
Mauriello, G., Ercoloni, D., La Storia, A., Casaburi, A., and Villani, F. (2004). "Development of polythene films for food packaging activated with an antilisterial bacteriocin from *Lactobacillus curvatus* 32Y," *J. Applied Microbiology*, 97, 314-322. DOI: 10.1111/j.1365-2672.2004.02299.X
Mertoğlu Elmas, G. (2017). "The effect of colorants on the content of heavy metals in recycled corrugated board papers," *BioResources* 12(2), 2690-2698. DOI: 10.15376/biores.12.2.2690-2698
Ministry of Health (2013). Survey of Selected Samples of Tattoo Inks for the Presence of Heavy Metals, Wellington145, New Zealand (www. health govt. nz.18.07. 2018)
Resolution AP, Council of Europe. (2002). "Paper and articles intended to come into contact with foodstuffs," EU and non EU countries.
Scott, W. E. (1996). *Principles of Wet End Chemistry*, TAPPI Press, Atlanta, GA, USA.
Skrzydlewska, E., Balcerzak, M., and Vanhaecke, F. (2003). "Determination of chromium, cadmium and lead in food-packaging materials by axial inductively coupled plasma time-of-flight mass spectrometry," *Analytica Chimica Acta* 479, 191-202.
Sönmez, S. (2017). "Development of printability of bio-composite materials using *Luffa cylindrica* fiber," *BioResources* 12(1), 760-773. DOI: 10.15376/biores.12.1.760-773

Sutter, J. (1994). "Innovative clean technologies case studies second year," (Project report), Cooperative Agreement. N. Cr-817670, Epa.600, R-94, 169.
Tiggelman, I. (2012). *Migration of Organic Contaminants through Paper and Plastic Packaging*, Master's Thesis, Stellenbosch University, Stellenbosch, South Africa.
Triantafyllou, V. I., Akrida-Demertzi, K., and Demertzis, P. (2007). "A study on the migration of organic pollutants from recycled paperboard packaging materials to solid food matrices," *Food Chem.* 101, 1759-1768. DOI: 10.1016/j.foodchem.2006.02.023
Vaarasalo, J. (1999). "Optical properties of paper," in: *Textbook of Pulp and Paper Testing*, J. Gullichsen and H. Paulapuro (eds.), Gummerus Printing, Jyväskylä, Finland, pp. 153-175.
WHO (1996). "Trace elements in human nutrition and health," World Health Organization Geneva.
Zalewski, S. (1994). *Design, Graphic Arts and Enviroment*, Master's Thesis, Rochester Institute of Technology, Rochester, NY, USA.
Zwinkels, J. C., and Noel, M. (2014). "CIE whiteness assessment of papers," in: *Impact of LED illumination, Conference: International Commission on Illumination CIE 27th Session*, Sun City, South Africa, pp. 323-330.

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